Article

Chinese Science Bulletin

Physical Chemistry

May 2013 Vol.58 No.13: 1529–1535
doi: 10.1007/s11434-013-5763-9

Adsorption of benzonitrile at the air/water interface studied by sum frequency generation spectroscopy

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Received June 11, 2012; accepted November 8, 2012; published online April 1, 2013

In this investigation, the adsorption of benzonitrile at the air/water interface was addressed using vibrational sum-frequency spectroscopy. Using *ppp* and *ssp* polarization combinations, the authors detected the symmetric stretching mode of the cyano (CN) group and calculated the orientation of benzonitrile at the interface. In addition, the adsorption isotherm was determined in terms of the hyperpolarizability element by varying the bulk benzonitrile concentration. The adsorption energy was obtained from fitting this isotherm. This work will add to our understanding of chemical processes relevant to retention, degradation, and photolysis of benzonitriles in the environment.

air/water interface, sum frequency generation, adsorption isotherm, benzonitrile

Citation: Liu A A, Huang Z, Deng G H, et al. Adsorption of benzonitrile at the air/water interface studied by sum frequency generation spectroscopy. Chin Sci Bull, 2013, 58: 1529–1535, doi: 10.1007/s11434-013-5763-9

Aqueous interfaces are of widespread importance in physics, chemistry, biology, and environmental science [1–3]. The adsorption of organic substances at the air/water interface has attracted tremendous attention in the field of environmental chemistry [4]. It is thought that the vapor/water interface could serve as an important retention domain in vadose-zone soil [5,6]. In addition to transport in vadose-zone soil, the effects of organic compounds on the properties of atmospheric aerosols are significant, and have become a focus of modern research in atmospheric chemistry [7,8]. Atmospheric gases adsorbed to a liquid aerosol surface participate in the heterogeneous reactions, which could play a significant role in removal or conversion of the organic contaminants [9,10]. Knowledge related to the adsorption thermodynamics and microscopic structure, such as the orientation of the organic molecules at the air/water interface, is necessary to better understand surface physicochemical properties including migration rate or surface reactivity [8].

Experimental characterization of the air/aqueous solution at the molecular level was difficult until the advent of nonlinear optical methods in the past few decades [11]. Because of their intrinsic surface sensitivity and selectivity, nonlinear optical methods including second harmonic generation (SHG) and sum-frequency generation vibrational spectroscopy (SFG-VS) provided the ability to explore the liquid surface microstructure spectroscopically [12,13]. These techniques have been widely employed to study the surface structure or the adsorption isotherms of water-soluble molecules at the vapor/water interface [14–16]. As a classic example, the air/acetonitrile aqueous solution interface was studied initially by Eisenthal and coworkers by SFG-VS [17]. They observed abrupt shifts in the CN vibrational frequency and in the orientation of the acetonitrile, which suggested that a phase transition occurs when varying the bulk acetonitrile concentration. Subsequently, the behavior of other molecules including DMSO, acetone, and methanol was also probed at aqueous interfaces [18–20].

Benzonitrile and its derivatives comprise an important

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class of organic compounds in the chemical industry. They are important intermediates in production of benzoguanamine, synthetic pesticides, fatty amines and acids, and could be precursors for synthesis of benzyl amine, which can be used as a pharmaceutical intermediate [21–23]. As herbicides, benzonitriles are deliberately introduced into the environment. The degradation of benzonitrile and its derivatives in the environment relies mainly on the biodegradation [22], photolysis [24,25] and photooxidative reactions, e.g., by OH or O_3 radicals [26]. In particular, theoretical evidences suggest that radicals such as OH and O_3 exhibit surface excess at the air/water interfaces as compared to the bulk, which implies that the air/water interface may serve as an important domain for the photooxidation reactions of nitriles [27]. In this regard, investigation into the surface structure and adsorption behavior of benzonitrile has fundamental importance for understanding the mechanism of heterogeneous reaction at the air/water interfaces. To date, only a few spectroscopic studies concerned with the interfacial structure and adsorption of benzonitrile derivatives are available. For example, the absolute orientation of different cyanophenol isomers at the air/aqueous surface was probed by SFG-VS, and the hydrogen bonding environment of the cyano (CN) group was analyzed [6]. In another publication, the absolute orientation of *m*-tolunitrile was determined by SFG-VS. The determination was based on orientation measurements of the methyl and cyano groups, which are two nonparallel, vibrationally-active chromophores in *m*-tolunitrile [28]. However, the adsorption behavior of benzonitrile at the air/aqueous interface has not yet been reported.

In this paper, we employed SFG-VS to study the adsorption behavior of benzonitrile at the air/aqueous interface. The approach is to directly and selectively probe the surface cyano group with different polarization schemes in order to extract simultaneous information about the orientation and concentration of the benzonitrile molecules at the surface. Furthermore, the adsorption isotherm is obtained by varying the bulk concentration, and the Gibbs free energy of adsorption is determined by fitting the adsorption isotherm.

1 Materials and methods

The details of the SFG-VS measurements have been described elsewhere [29]. Briefly, we used a 10 Hz and 23 ps SFG spectrometer laser system (EKSPLA) in a co-propagating configuration, with incident angles of 45°±1° and 55°±1° for the visible light and IR beams, respectively. The SFG signal was collected at the reflection geometry near 47°, within a small range of about 0.3°, which varied depending on the corresponding IR wavelength range in the SFG spectra. The efficiency of the detection system has been proven for the weak SFG signal of the air/water interface. A high- gain low-noise photomultiplier (Hamamatsu, PMT-R585) and a two-channel boxcar averaging system (Stanford Research Systems) were integrated into the EKSLPA system. The photomultiplier voltage was kept at a higher value for the measurement of air/water interfaces and a lower value for the Z-cut quartz surface because the signal intensity from the corresponding surfaces is different. The wavelength of the visible beam was fixed at 532 nm and the full range of the IR tunability was 1000–4300 cm^{-1}. Each scan was performed at a 2 cm^{-1} increment and was averaged over 200 laser pulses per point. The energies of the visible and IR beams were typically less than 230 and 150 μJ/pulse, respectively, in order to avoid any heat effects or photon damage to the liquid surfaces. Each spectrum was recorded at least two times and normalized against the SFG spectrum for Z-cut α-quartz. The detailed procedure for the normalization and the calculation were established in previous literature [29]. The spectral resolution was < 6 cm^{-1} over the whole IR tuning range. All measurements are carried out at a controlled room temperature (22.5±0.5°C) and humidity (<40%). Pure benzonitrile was purchased from Sigma-Aldrich (>98% HPLC grade) and was directly used without further purification. Standard Millipore treated ultrapure water (18.2 MΩ cm) was used as the solvent.

The theoretical framework of SFG has been well established [12,13,30]. Generally, the SFG intensity in the reflective direction is given by

$$I(\omega) = \frac{8\pi^3 \sec^2 \beta}{c^3 n(\omega) n(\omega_1) n(\omega_2)} \left| \chi_{\text{eff}}^{(2)} \right|^2 I_1(\omega_1) I_2(\omega_2), \quad (1)$$

where ω, ω_1, and ω_2 are the frequencies of the SF signal, visible, and IR laser beams, respectively. β is the reflected angle of the signal beam and $\chi_{\text{eff}}^{(2)}$ is the effective macroscopic second-order susceptibility of the interface. In order to eliminate influences of incident laser energy instabilities on the SFG signal, the signals are all normalized by dividing by the IR laser and visible laser energies. The effective macroscopic second-order susceptibility for the four independent polarization combinations generally used can be deduced from the seven nonzero macroscopic susceptibility tensors for an achiral rotationally isotropic interface ($C_{\infty v}$) [12,13,30]. Herein, only two of them are used and are given below:

$$\begin{aligned}
\chi_{\text{eff},ssp}^{(2)} &= L_{yy}(\omega) L_{yy}(\omega_1) L_{zz}(\omega_2) \sin\beta_2 \chi_{yyz}, \\
\chi_{\text{eff},ppp}^{(2)} &= -L_{xx}(\omega) L_{xx}(\omega_1) L_{zz}(\omega_2) \cos\beta \cos\beta_1 \sin\beta_2 \chi_{xxz} \\
&\quad - L_{xx}(\omega) L_{xx}(\omega_1) L_{zz}(\omega_2) \cos\beta \cos\beta_1 \sin\beta_2 \chi_{xxz} \\
&\quad + L_{zz}(\omega) L_{xx}(\omega_1) L_{xx}(\omega_2) \sin\beta \cos\beta_1 \cos\beta_2 \chi_{zxx} \\
&\quad + L_{zz}(\omega) L_{zz}(\omega_1) L_{zz}(\omega_2) \sin\beta \sin\beta_1 \sin\beta_2 \chi_{zzz}. \quad (2)
\end{aligned}$$

The consecutive subscripts indicate the polarization combinations; for instance *ssp* indicates that the SFG signal is *s* polarized, visible beam is *s* polarized, and IR beam is *p* polarized. It is so defined that the *xy* plane in the laboratory coordinate system $\lambda(x, y, z)$ is in the plane of the air/liquid

interface with z along the surface normal. The light beams propagate in the xz plane; p denotes the polarization of the optical field in the xz plane, while s the polarization perpendicular to the xz plane. $L_{ii}(i=x,y,z)$ are Fresnel coefficients determined by the refractive indices of the two bulk phases and the interface layer, and the incident and reflected angles [30].

The macroscopic sum frequency susceptibility tensors $\chi^{(2)}_{ijk}$ are related to the microscopic hyperpolarizability elements $\beta^{(2)}_{i'j'k'}$ in the molecular coordinate system $\lambda'(a,b,c)$ through the ensemble average, denoted by the $\langle\ \rangle$ operator, over all possible molecular orientations. They can be written as:

$$\chi^{(2)}_{ijk} = N_s \sum_{i'j'k'} \left\langle R_{ii'} R_{jj'} R_{kk'} \right\rangle \beta^{(2)}_{i'j'k'},$$
$$\beta^{(2)}_{i'j'k'} = \beta^{(2)}_{\mathrm{NR}} + \sum_q \frac{\beta^{(2)}_q}{\omega_{\mathrm{IR}} - \omega_q + i\Gamma_q}, \tag{3}$$

where $\beta^{(2)}_{\mathrm{NR}}$ represents the non-resonant contributions. ω_q is the vibrational frequency of the qth vibrational mode and Γ_q is the transverse relaxation rate, which describes the homogeneous broadening of the vibrational resonance.

2 Results and discussion

Quantitative polarization analysis can provide rich and detailed information of the structure, orientation, and surface concentration for benzonitrile at the air/aqueous interface [29]. SFG spectra at two polarization combinations, *ppp* and *ssp*, in the region from 2210 to 2270 cm^{-1} were taken at different bulk benzonitrile concentration in aqueous solution. A total of 11 solutions were prepared over a bulk concentration range from 5.0 to 45.0 mmol/L. The maximum concentration was limited by the aqueous solubility of benzonitrile. We present here spectra for only 4 of the 11 concentrations here in order to avoid unnecessary congestion, as shown in Figure 1. The spectra show only one evident peak located at around 2232 cm^{-1} in the scanning region, which is assigned to the symmetric stretch mode of the CN group. This assignment is in agreement with previous studies in which the mode of the CN group of a benzonitrile derivative, *m*-tolunitrile, at the air/aqueous solution interface was found to be located at 2234 cm^{-1} [28]. In addition, a shoulder of the major peak located at ~2270 cm^{-1} was observed for the 6 mmol/L *m*-tolunitrile solution, and the authors discussed several possibilities for the assignments of this feature. The most probable assignment possibility was that the shoulder could be a combination band of some modes in the 1000–1200 cm^{-1} energy region [28,31]. However, we did not observe this feature in the *ppp* or *ssp* SFG spectra of benzonitrile at any concentration, even when the scanning range was extended to 2300 cm^{-1} (not shown in the figure).

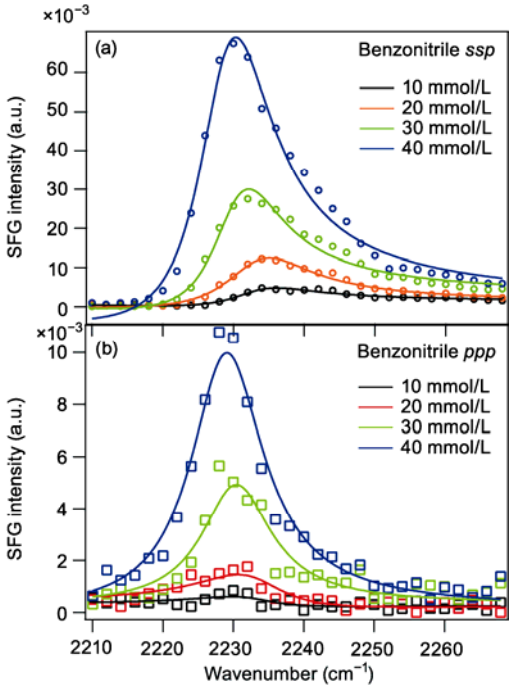

Figure 1 SFG spectra of the symmetric stretching mode of the CN group in benzonitrile at different bulk concentrations with (a) *ppp* and (b) *ssp* polarization combinations. The solid lines are results of the fitting procedure described in the text.

The spectra were globally fitted with the Lorentzian function as this provides a method to simply constrain the fitting parameters for the peak location and width at different polarizations, *ppp* and *ssp*. The detailed expression of the fitting equation is given by

$$I(\omega_{\mathrm{IR}}) = C + B\left|\chi^{(2)}_{\mathrm{NR,eff}} + \sum_q \frac{A_{q,\mathrm{eff}}}{\omega_{\mathrm{IR}} - \omega_q + i\Gamma_q}\right|^2. \tag{4}$$

The fitting parameters for spectra at different bulk concentrations are listed in Table 1, including the resonant frequency ω_q, the oscillator strength factors $A_{q,\mathrm{eff}}$, and the damping constant Γ_q, which is equal to the half width at half maximum of the peaks (HWHM) here. B and C are two fitting parameters related to the experimental configurations and the nonresonant susceptibility of the interfacial solvent molecules, respectively [29,30]. It is worth noting that, for dielectrics such as liquid interfaces, the nonresonant contribution to the SFG susceptibility is usually negligible compared to the resonant term, and thus the $\chi^{(2)}_{\mathrm{NR,eff}}$ term is considered to be zero [30,32].

First, we discuss the influence of the bulk concentration on the peak position. From the Lorentzian fitting of the CN spectra, we obtained the stretching frequencies of the surface CN group for different bulk concentrations, and can discuss the influence of the bulk composition on the energetics of the CN group at the interface. In Figure 2, we present the stretching frequency as a function of bulk

Table 1 Fitting parameters for SFG spectra of CN symmetric stretching peaks of air/benzonitrile aqueous interfaces

Concentration (mmol/L)	Peak position (cm^{-1})	HWHM (cm^{-1})	$A_{ssp,\mathrm{eff}}$ (a.u.)	$A_{ppp,\mathrm{eff}}$ (a.u.)	Orientation angle (°)
5.0	2234.5±0.8	7.9±0.8	0.017±0.196	0.244±0.040	–
10.0	2232.5±0.3	6.8±0.4	0.111±0.028	0.344±0.026	35.1±3.8
15.0	2233.9±0.3	6.9±0.4	0.192±0.035	0.643±0.036	35.9±2.6
20.0	2232.9±0.3	7.8±0.4	0.252±0.037	0.847±0.041	35.9±2.1
25.0	2232.0±0.4	7.7±0.5	0.431±0.056	1.105±0.076	33.2±2.9
30.0	2230.1±0.3	7.3±0.3	0.482±0.040	1.151±0.054	32.4±2.1
35.0	2230.1±0.2	5.6±0.3	0.479±0.053	1.400±0.064	34.6±2.0
37.5	2229.3±0.3	6.8±0.3	0.587±0.071	1.730±0.086	34.7±2.1
40.0	2228.9±0.2	6.5±0.3	0.644±0.050	1.650±0.065	33.2±1.7
42.5	2228.3±0.2	6.6±0.2	0.673±0.047	1.742±0.062	33.3±1.6
45.0	2228.1±0.3	6.4±0.3	0.580±0.073	1.734±0.087	34.8±2.2

concentration of benzonitrile. The dashed line is just a guide to the eyes, which indicates an evident trend of a monotonic decrease of the stretching frequency as the bulk concentration is increased. Similar shifts of the peak position were reported for the SFG spectrum of CH_3 symmetric stretching mode at the vapor/water-methanol mixture [19,33] or at the vapor/water-acetone mixture interface [20]. It is well accepted that the stretching frequency depends on the electron density localized in the CN bond, which suggests that higher electron density generally weakens the CN bond strength [17,34]. As a consequence, the vibrational frequency becomes red-shifted. In addition, the benzonitrile CN group in a polar solvent environment like water is usually hydrogen bonded with the water molecules [31]. The electron density of the CN bond is sensitive to the strength of the hydrogen bonds, with the water H atoms acting as electron acceptors [31]. Weakening of the hydrogen bonding leads to an increase in the CN bond electron density and further red-shifts the peak frequency. In this regard, it is reasonable to conclude that hydrogen bonding between benzonitrile and solvent water molecules become weaker as the interfacial density of benzonitrile is increased.

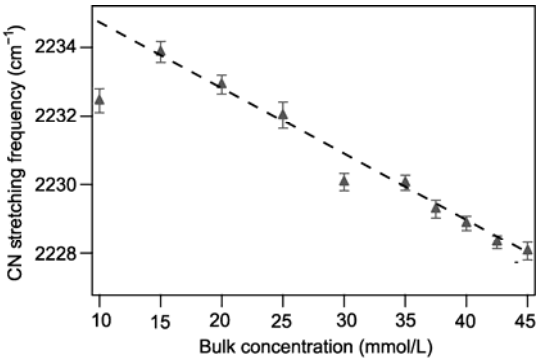

Figure 2 Stretching frequency of the CN group for benzonitrile at the air/aqueous solution interface as a function of the bulk concentration, which displays a monotonic decrease as the bulk concentration increases. The dashed line is a guide to eyes.

With the parameters listed in Table 1, we can further calculate the orientation of CN at the interface. The CN group can be generally approximated to have $C_{\infty v}$ symmetry because motions of the other parts of the molecule have little influence on the symmetric stretching mode of CN [35,36]. Therefore, it is valid to consider only three elements of the molecular hyperpolarizability, namely $\beta_{aac}=\beta_{bbc}=r\beta_{ccc}$. β_{aac} and β_{bbc} are the hyperpolarizability components with Raman polarizability and dipole moment derivatives perpendicular to the symmetry axis of CN, and β_{ccc} is the hyperpolarizability with Raman polarizability and dipole moment derivatives parallel to the symmetry axis [37]. The detailed expression of the macroscopic susceptibility tensor, $\chi^{(2)}_{ijk}$, for the symmetric stretching mode of CN in terms of the hyperpolarizability elements is written in the following form:

$$\begin{aligned}
\chi^{(2),\mathrm{ss}}_{xxz} &= \chi^{(2),\mathrm{ss}}_{yyz} = \frac{1}{2}N_s\beta^{(2)}_{ccc}\left[(1+r)\left\langle\cos\theta\right\rangle-(1-r)\left\langle\cos^3\theta\right\rangle\right],\\
\chi^{(2),\mathrm{ss}}_{xzx} &= \chi^{(2),\mathrm{ss}}_{zxx} = \chi^{(2),\mathrm{ss}}_{yzy} = \chi^{(2),\mathrm{ss}}_{zyy}\\
&= \frac{1}{2}N_s\beta^{(2)}_{ccc}\left[(1-r)\left\langle\cos\theta\right\rangle-(1-r)\left\langle\cos^3\theta\right\rangle\right],\\
\chi^{(2),\mathrm{ss}}_{zzz} &= N_s\beta^{(2)}_{ccc}\left[r\left\langle\cos\theta\right\rangle+(1-r)\left\langle\cos^3\theta\right\rangle\right].
\end{aligned} \tag{5}$$

For the present case, we take the value of $r = 0.26$, which has been used previously for the hyperpolarizability ratio of CN in *m*-tolunitrile [28]. Combined with eq. (3), it is easy to derive expressions for $\chi^{(2)}_{\mathrm{eff},ssp}$ and $\chi^{(2)}_{\mathrm{eff},ppp}$ as a function of θ and N_s. The oscillator strengths, $A^{(2)}_{ssp}$ and $A^{(2)}_{ppp}$, are plotted in Figure 3, through the ratio, $A^{(2)}_{ssp}/A^{(2)}_{ppp}$. The orientation θ was determined after using a δ distribution model for θ [30]. Following the treatment by Shen and coworkers, n' is directly calculated with the modified Lorentz model, which yields n'=1.15 [30]. With that, the orientation angle at different bulk concentrations was determined, as listed in Table 1.

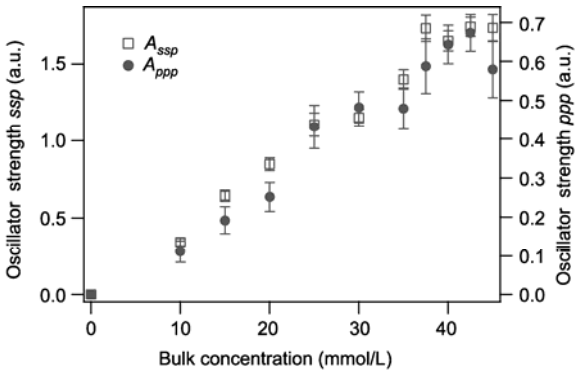

Figure 3 Oscillator strength of CN at *ppp* and *ssp* polarization combinations for different bulk concentrations. Under both polarization conditions, a monotonic increase was seen with increasing bulk concentration.

Figure 4 illustrates the orientation of CN at different bulk concentrations. We observe no significant changes in orientation even though the bulk concentration is close to the solubility limit for benzonitrile in aqueous solution, implying that the orientation is not sensitive to the surface coverage of the solute molecules over the range of investigated concentrations.

It is instructive to compare our result with that of similar nitrile molecules. Eisenthal and co-workers investigated the interfacial structure of the acetonitrile-water binary solution by SFG. They observed an abrupt change in the stretching frequency and the polarity orientation of CN at a mole fraction of 0.07 [17]. Somorjai and coworkers also studied the system by detecting the methyl group stretching mode with SFG-VS [38]. They found that the orientation of the methyl group does not change until the bulk mole fraction was much large-up to $x_{CH_3CN} = 0.2$ [38]. For the benzonitrile solution, the solubility limit of benzonitrile is so dilute that the maximum obtainable concentration only amounts to a mole fraction of less than 0.001. Over this range, we found that the orientation of CN is invariant. On the other hand, Richmond and coworkers investigated the influence of bulk concentration on the orientations of *m*-cyanophenol and *p*-cyanophenol [6]. The solubility of these benzonitrile derivatives is close to that of benzonitrile, and their orientations were also found to be invariant over the available concentration range. Hence, we infer that the chemical environment of interfacial benzonitrile is not effectively disturbed by such small changes in bulk concentration. In other words, the interaction between water and benzonitrile, which governs the orientation of benzonitrile, does not change over the dilute concentrations. This orientation is depicted in Figure 5, which is a schematic for the structure of the air/benzonitrile aqueous solution interface.

We were also able to determine the surface number density, N_s, after subtracting interference arising from molecular orientation effects. It can be directly derived from eqs. (3) and (5) that

$$N_s = 2A_{ssp}\beta^{(2)}_{ccc} \Big/ L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2) \times \sin\beta_2\left[(1+r)\langle\cos\theta\rangle - (1-r)\langle\cos^3\theta\rangle\right]. \quad (6)$$

It is reasonable to assume that the hyperpolarizability element, β_{ccc}, does not vary with the bulk concentration. Thus, the surface density, N_s, in terms of β_{ccc} can be extracted for different bulk compositions, as illustrated in Figure 6. With this plot, the adsorption isotherm of benzonitrile at the air/water interface is obtained. The adsorption at the air/liquid interfaces has usually been described by the classic Langmuirian model, where the surface density number of the solute could be written as [39]:

$$N_s = \frac{N_s^{max} K C_{bulk}}{C_{water} + K C_{bulk}} \approx \frac{N_s^{max} C_{bulk}}{C_{bulk} + 55.5M \exp(\Delta G_{ads}/RT)}, \quad (7)$$

where, N_s^{max} is the maximum obtainable surface number density, K is the equilibrium constant for occupying a surface site, C_{bulk} is the bulk concentration of the solute, and C_{water} is the mole concentration of water, which is approximated to be 55.5 mol/L in dilute solution. The solid line in

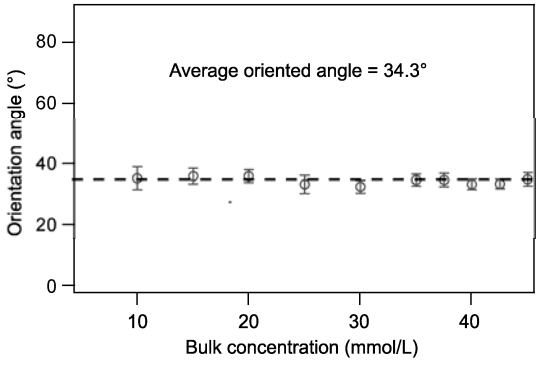

Figure 4 Calculated orientation angles of the CN chromophore at the air/water interface as a function of the bulk concentration of the benzonitrile solution. The orientation remained constant within the error bars with an average value of 34.3°, indicated by the dashed line.

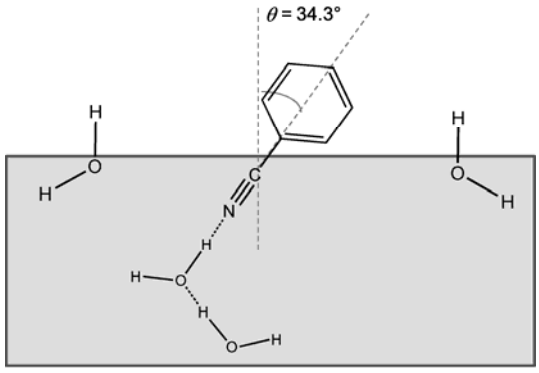

Figure 5 Schematic for the interfacial structure of the air/benzonitrile aqueous solution interface. The benzonitrile is hydrogen bonded with the water, and oriented at 34.3° with respect to the surface normal.

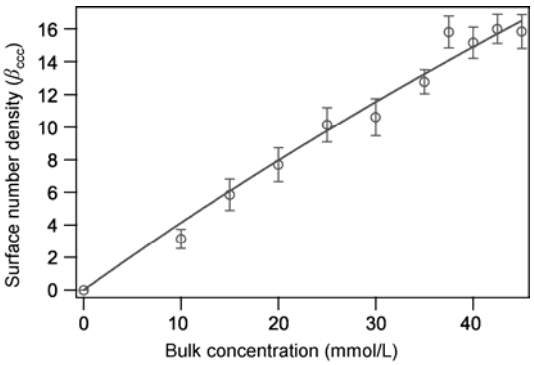

Figure 6 Surface number density of CN groups in terms of the hyperpolarizability element, β_{ccc}, at the air/benzonitrile solution interface for different bulk concentrations. The solid line is the fitting result with a Langmuir adsorption isotherm, yielding a value of −13.5±0.5 kJ/mol for the Gibbs free energy of adsorption.

Figure 5 is a fitting result to this Langmuir model (eq. (7)), yielding a value of −13.5±0.5 kJ/mol for the Gibbs free energy of adsorption. This value is comparable to that of some analogous organic molecules such as methylaniline and methylphenol, whose adsorption free energies at the air/aqueous interface are −14.7±1.4 kJ/mol and −16.0±0.1 kJ/mol, respectively [40].

3 Conclusions

As has been reported, the air/water interface plays an important role in retention of organic contaminants; moreover, better understanding of the degradation mechanism for such contaminants requires detailed knowledge of the microscopic structure and the fundamental thermodynamic behavior at the interface. We have investigated the adsorption of benzonitrile at the air/water interface by means of the SFG technique and have discussed the influence of the bulk concentration on microscopic aspects of the interfacial species, including the orientation as well as the energetics of the interfacial CN moiety. Our studies reveal that the CN orientation angle is around 34.3° and remains unchanged over the whole range from very dilute concentration to the solubility limit of benzonitrile. This result implies the chemical environment is not significantly affected as the bulk composition varies. Moreover, we also obtained the adsorption isotherm and the Gibbs free energy of adsorption. It was found that the adsorption behavior of benzonitrile followed the classic Langmuir model. Fitting the data with this model yielded a value of −13.5±0.5 kJ/mol for the Gibbs free energy of benzonitrile adsorption at the air/aqueous interface. Our work may shed light on related issues in environmental science.

This work was supported by the Main Direction Program of Knowledge Innovation of Chinese Academy of Sciences (*KJCX-EW-W09*) *and the National Natural Science Foundation of China* (*91027042, 21073199*). *The authors would also thank Prof. WANG HongFei for discussions.*

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